

PATENT SPECIFICATION

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(54) ELECTROLYSIS ELECTRODE FOR OXYGEN EVOLUTION

(71) We, ELECTRONOR CORPORATION, a Panamanian Corporation of Apartado 6307, Panama City, Panama, do hereby declare the invention, for which we 5 pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

In various electrochemical processes, for 10 example in the production of chlorine and other halogens, the production of chlorates, the electrolysis of other salts which undergo decomposition under electrolysis conditions and other electrolytic processes, it has recently 15 become commercially possible to use dimensionally stable electrodes in place of graphite. These dimensionally stable electrodes usually have a film forming valve metal base, for example of titanium, tantalum, zirconium, 20 aluminium, niobium or tungsten, which has the capacity to conduct current in the cathodic direction and to resist the passage of current in the anodic direction and are sufficiently 25 resistant to the electrolyte and conditions used within an electrolytic cell, for example, in the production of chlorine and caustic soda, to enable them to be used as electrodes in electrolytic processes. In the anodic direction, however, the resistance of the valve metals 30 to the passage of current increases rapidly, due to the formation of an oxide layer thereon, so that it is no longer possible to conduct current to the electrolyte in any substantial amount without a substantial increase in voltage which 35 makes continued use of uncoated valve metal electrodes in an electrolytic process uneconomical.

It is, therefore, customary to apply electrically 40 conductive electrocatalytic coatings to these dimensionally stable valve metal electrode bases. The electrode coatings must have the capacity to continue to conduct current to the electrolyte over long periods of time

without becoming passivated and in chlorine production, must have the capacity to catalyze the formation of chlorine molecules from the chloride ions at an anode. The coatings must be electroconductive and electrocatalytic and must adhere firmly to the valve metal base over long periods of time under cell operating conditions.

Commercially available coatings contain a catalytic metal or oxide from the platinum group metals, i.e., platinum, palladium, iridium, ruthenium, rhodium or osmium, and a binding or protective agent such as titanium dioxide, tantalum pentoxide and other valve metal oxides in an amount sufficient to protect the platinum group metal or oxide from being removed from the electrode in the electrolysis process and to bind the platinum group metal or oxide to the electrode base. The binding and protective metal oxide is usually in excess of the platinum group metal or oxide. Anodes of this nature have been described, for example, in British Patent No. 1,231,280.

In anodes for the recovering of metals from uses by electrowinning, a continual source of difficulty has been the selection of a suitable material for the anode. The requirements are insolubility, resistance to the mechanical and chemical effects of oxygen liberated on the surface of the anode, low oxygen overvoltage, and resistance to breakage in handling. Lead anodes containing from 6 to 15 per cent antimony have been used in most plants. Such anodes are attacked by chloride ions if present in the electrolyte. This is the case at the huge plant at Chuquicamata, Chile, where it is necessary to remove cupric chloride dissolved from an ore by passing the solution over cement copper, reducing the cupric to insoluble cuprous chloride. At this plant there was also developed an anode of a copper-silicon alloy, called the Chilex anode, used in a portion of the tank-room. It has a longer life than lead

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anodes but raises the power consumption because of greater resistance and greater oxygen overvoltage.

Attempts to use mixed oxide coatings such as RuO_2 — TiO_2 for oxygen evolution have not been satisfactory in commercial use because passivation takes place after 200 to 1000 hours of operation at a current density of 1.2 KA per m^2 . The use of a Ta_2O_5 — RuO_2 mixed oxide coating improves the electrocatalytic activity and the life of the anode somewhat but not enough for commercial use. The use of a TiO_2 — IrO_2 coating has lower electrocatalytic activity.

According to this invention, an electrode for use in an electrochemical process comprises an electrically conductive base provided over at least a portion of its outer surface with a coating comprising a mixed crystal material of tantalum oxide and iridium oxide, the proportion of tantalum to iridium calculated as metal in the material being from 1:1 to 0.34:1 by weight.

The coating may extend over as little as 5% of the outer surface of the electrode but it preferably covers from 50% to 100% of the active face of the electrode.

The electrode base may be made of any electrically conductive material such as metals and alloys thereof such as iron, nickel, lead or copper, but is preferably a valve metal. Valve metals, or film forming metals as they are also called, are metals which have the capacity to conduct current in the cathodic direction and to resist the passage of current in the anodic direction. Examples are tungsten, titanium, tantalum, niobium, aluminium or zirconium or alloys of two or more of these metals. The valve metal base may be provided with an intermediate layer such as an oxide of the valve metal or a coating of another metal such as platinum group metals. The base may be of a valve metal together with at least one other metal having a low hydrogen overvoltage, such as alloy of titanium with iron, cobalt, nickel, palladium, vanadium or molybdenum, or a mixture of two or more of these metals; or the base may be of titanium with at least one metal suitable to form with the titanium a protective oxide film even in acid solution, such as an alloy of titanium with niobium, tantalum, zirconium or mixtures of two or more of said metals.

In a preferred embodiment of the invention, the electrically conductive base is an alloy of a valve metal with a platinum group metal which has resistance to corrosion by acid electrolytes encountered in the use of the electrodes such as 5% to 15% sulphuric acid or 1% to 5% hydrochloric acid. A particularly useful alloy is titanium containing from 0.1% to 0.20% by weight of palladium. This corrosion resistance of the base prevents chipping off of the coating even if the anode is im-

mersed for a few hours in an acid electrolyte without anodic polarization.

In another embodiment of the invention, the coating containing tantalum oxide and iridium oxide is doped with an oxide of a metal with a valency of less than +4 to increase the catalytic activity for oxygen evolution without adversely affecting the mechanical properties of the coating.

It is believed that the conductivity of the Ta_2O_5 — IrO_2 mixed crystal material is of the *n* type and that the addition of the doping metal oxide reverses the type of conductivity from "n type" to "p type" which improves the anodic process by producing electronic holes.

The doping metal oxide may be present in the coating in amounts ranging from 0.5% to 5.0%, preferably from 1.5% to 3.0%, by weight of the doping metal oxide and the Ta_2O_5 — IrO_2 mixed crystal material, all the components of the percentage being calculated as metal. Examples of suitable doping metal oxides are alkaline earth metals such as calcium, magnesium, barium and members of Groups VIII, VI A and VII A of the periodic Table such cobalt, iron and nickel, chromium, molybdenum, or manganese.

The increase in the catalytic activity of the doped coatings is shown by the lower anode potential of doped anodes compared with undoped anodes after 8000 hours of operation of the anodes under identical working conditions. The doping seems to have no adverse effect on the mechanical properties of the coating as there is no coating loss in either instance even after 8000 hours operation.

Electrodes in accordance with the invention are particularly useful for electrolytic processes such as cathodic protection, electroflotation, organic electrosynthesis such as hydrodimerization of acrylonitrile and most particularly the electrowinning of metals. The electrodes have a high electrocatalytic activity and a very low passivation rate of a few millivolts per month at a current density of 1.2 to 2.0 KA per m^2 and a negligible weight loss if kept under anodic polarization.

The electrodes in accordance with the invention may be prepared by a method which, in accordance with another aspect of the invention, comprises applying to an electrically conductive electrode base a solution of suitable relative quantities of a thermally decomposable compound of tantalum and a thermally decomposable compound of iridium, drying the coated electrode base by evaporation of the solvent and then heating the dried electrode base in the presence of oxygen to form the oxide coating.

The heating step is preferably effected at temperatures of from 350° to 600°C, the optimum temperature being from 500° to 550°C. At temperatures below 350°C, the oxidation may not be completed or may require

too long a heating time and at temperatures above 600°C, the electrode base is likely to be subjected to distortions and/or destruction by the high temperatures.

5 The preliminary drying step is preferably effected by gentle heating in air to evaporate the solvent and codeposit the metal compounds. However, any convenient evaporation procedure may be used to remove the solvent such as standing under reduced pressure.

10 In a preferred example of the process, the coating is applied in multiple coats with short periods of intermediate heating in the presence of oxygen such as from 500° to 550°C for 15 from 5 to 15 minutes with a longer final heating in the presence of oxygen after the last coat such as from 500° to 550°C for from 45 minutes to 1½ hours. The coating obtained thereby is very adherent and quite 20 uniform.

25 Electrodes in accordance with the invention are particularly useful for the electrowinning processes used in the production of various metals because they do not add to the bath impurities which deposit on the cathode, with the metal being won, and thereby contaminate the refined metal, as do anodes of from example lead containing antimony and bismuth which produce impure cathode refined metals. 30 Moreover, their resistance to the acid solutions and oxygen evolution and their excellent

anode potential makes them desirable for this use.

The invention will now be further explained with reference to a number of examples. In all of these examples except Examples II and VI electrically conductive plates are produced having coatings of mixed crystal material of tantalum oxide and iridium oxide, the proportion of tantalum to iridium calculated as metal in the material being from 1:1 to 0.34:1 by weight. Example II is given for comparison purposes only and Example VI is concerned with an electrolytic process.

EXAMPLE I.

24 Titanium plates 10 mm by 10 mm were etched in boiling 20% hydrochloric acid for sixty minutes and were then thoroughly washed with water. The plates were then coated with an aqueous solution of the compositions of Table I in from 12 to 15 coats. After the application of each coat, the plates were dried and then heated for 10 minutes at from 450°C to 600°C in an oven with forced air circulation and then allowed to air cool. After the last coat, the plates were heated in the oven at the same temperature for 1 hour and were then air cooled. The values of Table I are calculated as weight of free metal. The tantalum chloride was used as a solution in 20% hydrochloric acid.

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TABLE I

| Sample No. | Coating Composition in mg | Heating temp in °C |
|----------------|-------------------------------|--------------------|
| A ₁ | TaCl ₅ - 16 | 450 |
| A ₂ | + IrCl ₃ - 16 | 500 |
| A ₃ | for each sample | 550 |
| A ₄ | | 600 |
| B ₁ | TaCl ₅ - 13.10 | 450 |
| B ₂ | + IrCl ₃ - 16.0 | 500 |
| B ₃ | for each sample | 550 |
| B ₄ | | 600 |
| C ₁ | TaCl ₅ - 10.70 | 450 |
| C ₂ | + IrCl ₃ - 16.0 | 500 |
| C ₃ | for each sample | 550 |
| C ₄ | | 600 |
| D ₁ | TaCl ₅ - 8.6 | 450 |
| D ₂ | + IrCl ₃ - 16.0 | 500 |
| D ₃ | for each sample | 550 |
| D ₄ | | 600 |
| E ₁ | TaCl ₅ - 6.85 | 450 |
| E ₂ | + IrCl ₃ - 16.0 | 500 |
| E ₃ | for each sample | 550 |
| E ₄ | | 600 |
| F ₁ | TaCl ₅ - 5.46 | 450 |
| F ₂ | + IrCl ₃ - 16.0 | 500 |
| F ₃ | for each sample | 550 |
| F ₄ | | 600 |

5 The anode potential for each anode was determined by electrolysis of 10% by weight sulphuric acid at 60°C and a current density of 1.2 KA/m². The initial anode potential (against NHE) and the anode potential after 3000 and 6000 hours was determined and the coating loss was then determined. The results are set out in Table II.

TABLE II

| Sample No. | Anode Potential V(NHE) | | | Coating Weight loss mg/cm ² |
|----------------|------------------------|----------------|-----------------|---|
| | initial value | after 3000 hrs | after 6000 hrs. | |
| A ₁ | 1.50 | 1.68 | 1.77 | 0.2 |
| A ₂ | 1.52 | 1.62 | 1.70 | 0.0 |
| A ₃ | 1.52 | 1.62 | 1.70 | 0.0 |
| A ₄ | 1.52 | 1.62 | 1.77 | 0.0 |
| B ₁ | 1.51 | 1.63 | 1.73 | 0.6 |
| B ₂ | 1.51 | 1.62 | 1.68 | 0.0 |
| B ₃ | 1.52 | 1.62 | 1.68 | 0.0 |
| B ₄ | 1.51 | 1.63 | 1.79 | 0.0 |
| C ₁ | 1.50 | 1.65 | 1.70 | 0.3 |
| C ₂ | 1.51 | 1.63 | 1.64 | 0.0 |
| C ₃ | 1.52 | 1.58 | 1.63 | 0.0 |
| C ₄ | 1.52 | 1.63 | 1.73 | 0.0 |
| D ₁ | 1.49 | 1.61 | 1.68 | 0.5 |
| D ₂ | 1.50 | 1.60 | 1.62 | 0.0 |
| D ₃ | 1.52 | 1.58 | 1.62 | 0.0 |
| D ₄ | 1.52 | 1.60 | 1.67 | 0.0 |
| E ₁ | 1.52 | 1.62 | 1.66 | 0.2 |
| E ₂ | 1.50 | 1.60 | 1.61 | 0.0 |
| E ₃ | 1.52 | 1.56 | 1.61 | 0.0 |
| E ₄ | 1.52 | 1.63 | 1.67 | 0.5 |
| F ₁ | 1.48 | 1.56 | 1.73 | 0.9 |
| F ₂ | 1.47 | 1.53 | 1.74 | 0.6 |
| F ₃ | 1.47 | 1.52 | 1.77 | 1.2 |
| F ₄ | 1.49 | 1.60 | 1.80 | 1.3 |

5 The results of Table II show that the electrodes in accordance with the invention have high electrocatalytic activity and a very low passivation rate and that the weight loss of the coating is negligible when within the preferred limits of the invention. It should be noted that the weight ratio of Ta to Ir for samples F₁ to F₄ is about 0.34. Optimum values are obtained in the heating range of 10 from 500°—550°C.

EXAMPLE II.

For comparative purposes, electrodes were prepared as follows. Titanium plates 10 mm

by 10 mm were etched in boiling 20% hydrochloric acid for sixty minutes and were then 15 thoroughly washed with water. The plates were then coated with an aqueous solution of the compositions of Table III in 12 to 15 coats. After the application of each coat, the plates were dried and then heated for 10 minutes 20 at from 450°C to 550°C in an oven with forced air circulation and then allowed to air cool. After the last coat, the plates were heated in the oven at the same temperature for 1 hour and were then air cooled. The values of 25 Table III are calculated as weight of free metal.

TABLE III

| Sample No. | Coating composition in mg | heating temp in °C |
|------------|--|-----------------------|
| 1 | TiCl ₃ — 19.5 | 450 |
| | RuCl ₃ · 3H ₂ O — 16.0 | |
| 2 | TiCl ₃ — 10.7 | 450 |
| | RuCl ₃ · 3H ₂ O — 16.0 | |
| 3 | TaCl ₅ — 19.5 | 450 |
| | RuCl ₃ · 3H ₂ O — 16.0 | |
| 4 | TaCl ₅ — 10.7 | 450 |
| | RuCl ₃ · 3H ₂ O — 16.0 | |
| 5 | TiCl ₃ — 19.5 | 500 |
| | IrCl ₃ — 16.0 | |
| 6 | TiCl ₃ — 19.5 | 550 |
| | IrCl ₃ — 16.0 | |
| 7 | TiCl ₃ — 10.7 | 500 |
| | IrCl ₃ — 16.0 | |
| 8 | TiCl ₃ — 10.7 | 550 |
| | IrCl ₃ — 16.0 | |

30 The anode potential for each anode was then determined by electrolysis of 10% by weight sulphuric acid at 60°C at a current density of 1.2 KA/m². The initial anode

potential and the anode potential after 600, 1000 or 1200 hours are reported in Table IV. The final loss of the coating was determined at the end of the test. 35

TABLE IV

| Sample No. | Anode potential (NHE) in Volts after | | | | coating loss in mg/cm ² |
|------------|--------------------------------------|-------|--------|--------|------------------------------------|
| | initial | 600 h | 1000 h | 1200 h | |
| 1 | 1.48 | — | 2.00 | 2.5 | 0 |
| 2 | 1.47 | — | 1.95 | 2.2 | 0 |
| 3 | 1.46 | — | 1.85 | 2.09 | 0 |
| 4 | 1.45 | — | 1.79 | 2.00 | 0 |
| 5 | 1.52 | 1.82 | 1.86 | — | 0 |
| 6 | 1.52 | 1.89 | 1.93 | — | 0 |
| 7 | 1.51 | 1.81 | 1.85 | — | 0 |
| 8 | 1.52 | 1.85 | 1.90 | — | 0 |

5 The results of Table IV show that RuO₂—TiO₂ coated electrodes become passivated after only 1000 hours and the Ta₂O₅—RuO₂ coated electrodes are only slightly improved and the TiO₂—IrO₂ coated electrodes are no better.

EXAMPLE III.
10 plates of titanium plates containing 0.15% of palladium (10 x 10 mm) were sand-

blasted and then etched in refluxing 20% hydrochloric acid for 60 minutes. The plates were then coated with the compositions of Table V. The compositions were applied in 10
15 to 20 coats with intermediate heating at 450°C for 10 minutes in an oven with forced air circulation and cooling in air. The final heating was effected at the temperatures in Table V for 1 hour followed by air cooling.

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TABLE V

| Sample No. | Coating compositions in mg of free metal | Final heating in °C |
|------------|--|---------------------|
| AA | TaCl ₅ — 16 + | 500 |
| BB | IrCl ₃ — 16 | 550 |
| CC | TaCl ₅ — 13.10 + | 500 |
| DD | IrCl ₃ — 16.0 | 550 |
| EE | TaCl ₅ — 10.70 + | 500 |
| FF | IrCl ₃ — 16.0 | 550 |
| GG | TaCl ₅ — 8.60 + | 500 |
| HH | IrCl ₃ — 16 | 550 |
| II | TaCl ₅ — 6.85 + | 500 |
| JJ | IrCl ₃ — 16 | 550 |

The anode potentials and coating weight loss were determined as in Example I and the results are reported in Table VI.

TABLE VI

| Sample No. | Anode Potential in V (NHE) | | | Coating weight loss in mg/cm ² after 2000 hs. |
|------------|----------------------------|---------------|---------|--|
| | initial value | after 3000 hs | 6000 hs | |
| AA | 1.52 | 1.62 | 1.69 | 0.0 |
| BB | 1.51 | 1.63 | 1.70 | 0.0 |
| CC | 1.51 | 1.62 | 1.68 | 0.0 |
| DD | 1.52 | 1.62 | 1.68 | 0.0 |
| EE | 1.51 | 1.63 | 1.65 | 0.0 |
| FF | 1.52 | 1.58 | 1.64 | 0.0 |
| GG | 1.50 | 1.59 | 1.63 | 0.0 |
| HH | 1.52 | 1.58 | 1.62 | 0.0 |
| II | 1.50 | 1.57 | 1.60 | 0.0 |
| JJ | 1.52 | 1.58 | 1.60 | 0.0 |

5 The results of Table VI show that the electrodes of the invention with a titanium-palladium alloy base have excellent electro-catalytic activity and low passivation rates.

EXAMPLE IV.

10 To demonstrate the improved corrosion resistance of a preferred titanium-palladium alloy base, 10 plates made of titanium containing 0.15% by weight of palladium (10 x 10 mm) were sand-blasted and then etched in

15 refluxing 20% hydrochloric acid for 60

minutes. The plates were then coated with the compositions of Table V using the procedure of Example III. The anode potential was determined for each electrode by electrolysis of 10% sulphuric acid at 60°C and a current density of 1.2 KA/m². The initial anode potential and the value after 1000 and 2000 hours and the coating weight loss after 2000 hours was determined. Moreover, the current was halted for 15 minutes in each 24 hour period without removing the electrode from the acid bath. The results are set out in Table VII.

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TABLE VII

| Sample No. | Anode Potential V (NHE) | | | Coating weight loss in mg/cm ² |
|------------|-------------------------|----------|----------|---|
| | initial value | 1000 hs. | 2000 hs. | |
| AA | 1.52 | 1.66 | 1.68 | 0.2 |
| BB | 1.51 | 1.66 | 1.67 | 0.3 |
| CC | 1.51 | 1.57 | 1.62 | 0.3 |
| DD | 1.52 | 1.58 | 1.60 | 0.3 |
| EE | 1.50 | 1.56 | 1.58 | 0.3 |
| FF | 1.52 | 1.56 | 1.58 | 0.3 |
| GG | 1.50 | 1.55 | 1.56 | 0.3 |
| HH | 1.52 | 1.54 | 1.56 | 0.3 |
| II | 1.52 | 1.54 | 1.55 | 0.3 |
| JJ | 1.51 | 1.55 | 1.55 | 0.3 |

The results of Table VII show that the electrodes of the invention having a titanium-palladium alloy base have excellent electrocatalytic activity and low passivation rates and the coating does not chip off even without anodic polarization.

EXAMPLE V.
10 titanium plates (20 x 20 mm) were etched in refluxing 20% hydrochloric acid for 60 minutes and after being thoroughly washed with water, the plates were coated with an aqueous solution containing 2.01 mg (as free metal) of $TaCl_5$, 5.2 mg (as free metal) of $IrCl_3$ and 0.0394 ml of hydrochloric acid. The

solution was applied in 12 coats with intermediate heating and cooling and a final heating as described in Example I.

The coated titanium plates were used as anodes in cells for the recovery of zinc from an aqueous electrolyte containing 100 g/litre of $ZnSO_4$ (as free metal), 10% sulphuric acid and 10 to 50 ppm of glue. The cathode was a pure aluminium sheet with a smooth surface and the electrolyte gap was 10 mm. The current density was 500 A/m² and the electrolyte temperature was 35°C. The anode potential, loss of coating, zinc thickness on the cathode and the morphology of the zinc deposit are reported in Table VIII.

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TABLE VIII

| Test No. | Anode potential V(NHE) | Coating weight loss | Zn deposit thickness in mm | Zn deposit morphology |
|----------|------------------------|---------------------|----------------------------|-----------------------|
| 1 | 1.47 | 0 | 3.2 | smooth |
| 2 | 1.48 | 0 | 3.5 | „ |
| 3 | 1.49 | 0 | 4.1 | „ |
| 4 | 1.47 | 0 | 3.5 | „ |
| 5 | 1.48 | 0 | 3.1 | „ |
| 6 | 1.50 | 0 | 3.0 | „ |
| 7 | 1.49 | 0 | 3.0 | „ |
| 8 | 1.50 | 0 | 4.1 | „ |
| 9 | 1.48 | 0 | 4.1 | „ |
| 10 | 1.47 | 0 | 4.0 | „ |

The cathodic current efficiency was found to be 92—95% in all cases and the purity of the zinc deposit was 99.9999%.

EXAMPLE VI.

Using the procedure of Example V, 5 titanium plates (20 x 20 cm) were coated with the composition of Example V. The coated plates were used as anodes in a cell for recovery

10 of copper from an aqueous electrolyte con-

taining 100 g/litre (as free metal) of CuSO_4 and 10 g/litre of sulphuric acid and the cathode was a smooth steel plate. The electrolyte gap was 15 mm and the bath temperature was 60°C. The current density was 500 A/m². The anode potential, loss of coating and copper thickness and morphology of the copper deposit are reported in Table 1X.

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TABLE IX

| Test No. | Anode potential V (NHE) | Coating weight loss | Cu deposit thickness in mm | Cu deposit morphology |
|----------|-------------------------|---------------------|----------------------------|-----------------------|
| 1 | 1.47 | 0 | 4.5 | smooth |
| 2 | 1.50 | 0 | 4.5 | „ |
| 3 | 1.48 | 0 | 5.8 | „ |
| 4 | 1.47 | 0 | 4.1 | „ |
| 5 | 1.49 | 0 | 5.8 | „ |

The cathodic current efficiency was found to be 100% in all cases and the purity of the copper was 99.9999%.

EXAMPLE VII.

25 16 titanium coupons (20 x 20 mm) were etched in boiling azeotropic 20% hydrochloric acid for 40 minutes and were

thoroughly washed. The coupons were then coated with the composition of Table X in 20 coats. After the first 19 coats, the coupons were heated in a forced air circulation oven at 500°C and then were air cooled. The last heating was at 500 or 550°C for 1 hour followed by air cooling.

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TABLE X

| Specimen No. | Liquid Coating per each titanium sheet coupon | | | Ir as metal gm/m ² |
|---------------|---|----------------|--|-------------------------------|
| 1, 1A, 1B, 1C | TaCl ₅ | 2.077 mg as Ta | | |
| | IrCl ₃ | 3.2 , , Ir | | 16 |
| | CaCl ₂ . 6H ₂ O | 0.053 , , Ca | | |
| | HCl | 0.0413 mls | | |
| 2, 2A, 2B, 2C | TaCl ₅ | 2.000 mg as Ta | | |
| | IrCl ₃ | 3.2 , , Ir | | 16 |
| | CaCl ₂ . 6H ₂ O | 0.13 , , Ca | | |
| | HCl | 0.0394 mls. | | |
| 3, 3A, 3B, 3C | TaCl ₅ | 1.92 mg as Ta | | |
| | IrCl ₃ | 3.2 , , Ir | | 16 |
| | CaCl ₂ . 6H ₂ O | 0.21 , , Ca | | |
| | HCl | 0.0374 mls. | | |
| 4, 4A, 4B, 4C | TaCl ₅ | 1.87 mg as Ta | | |
| | IrCl ₃ | 3.2 , , Ir | | 16 |
| | CaCl ₂ . 6H ₂ O | 0.26 , , Ca | | |
| | HCl | 0.0362 mls. | | |

The samples were then tested in 10% sulphuric acid at 60°C with an anodic current density of 1.2 KA/m² to determine the anode

potential and coating loss after 3500 hours. 5
The results are shown in Table XI.

TABLE XI

| Specimen No. | Temperature final heat treatment | Ca content % by wt. | Anode Potential | | Weight loss mg/cm ² |
|--------------|----------------------------------|---------------------|-----------------|-----------------------|--------------------------------|
| | | | initial value | after 2500 hs. V(NHE) | |
| 1 | 500°C | 1 | 1.51 | 1.55 | 0 |
| 1A | " | | 1.51 | 1.56 | " |
| 1B | 550°C | 1 | 1.51 | 1.56 | " |
| 1C | " | | 1.51 | 1.56 | " |
| 2 | 500°C | 2.5 | 1.50 | 1.51 | " |
| 2A | " | | 1.51 | 1.51 | " |
| 2B | 550°C | 2.5 | 1.50 | 1.52 | " |
| 2C | " | | 1.50 | 1.52 | " |
| 3 | 500°C | 4.0 | 1.51 | 1.58 | " |
| 3A | " | | 1.52 | 1.58 | " |
| 3B | 550°C | 4.0 | 1.51 | 1.58 | " |
| 3C | " | | 1.51 | 1.58 | " |
| 4 | 500°C | 5.0 | 1.51 | 1.60 | " |
| 4A | " | | 1.52 | 1.60 | " |
| 4B | 550°C | 5.0 | 1.52 | 1.65 | " |
| 4C | " | | 1.52 | 1.65 | " |

EXAMPLE VIII. with the composition of Table XII with the 5
 Using the procedure of Example VII, same heatings.
 20 x 20 mm titanium coupons were coated

TABLE XII

| Specimen No. | <i>Liquid Coating per each titanium sheet coupon</i> | | <i>Ir as metal gm/m²</i> |
|---------------|--|-----------------|-------------------------------------|
| 1, 1A, 1B, 1C | TaCl ₅ | 2.077 mg. as Ta | |
| | IrCl ₃ | 3.200 , , Ir | 16 |
| | CoCl ₂ . 6H ₂ O | 0.053 , , Co | |
| | HCl | 0.0412 mls. | |
| 2, 2A, 2B, 2C | TaCl ₅ | 2.000 mg. as Ta | |
| | IrCl ₃ | 3.200 , , Ir | 16 |
| | CoCl ₂ . 6H ₂ O | 0.13 , , Co | |
| | HCl | 0.0394 mls. | |
| 3, 3A, 3B, 3C | TaCl ₅ | 1.92 mg. as Ta | |
| | IrCl ₃ | 3.200 mg , Ir | 16 |
| | CoCl ₂ . 6H ₂ O | 0.21 , , Co | |
| | HCl | 0.0374 mls. | |
| 4, 4A, 4B, 4C | TaCl ₅ | 1.87 , , Ta | |
| | IrCl ₃ | 3.200 , , Ir | 16 |
| | CoCl ₂ . 6H ₂ | 0.26 , , Co | |
| | HCl | 0.0362 mls. | |

The anode potentials and the coating losses after 8000 hours were determined as in Example VII and the results are reported in Table XIII.

TABLE XIII

| Specimen | Temperature final heat treatment | Co content % by wt. | Anode Potential | | Coating weight loss mg/cm ² |
|----------|--|------------------------|-------------------|-------------------|---|
| | | | initial V(NHE) | after 8000 hs. | |
| 1 | 500°C | 1 | 1.52 | 1.56 | 0 |
| 1A | ," | ," | 1.52 | 1.56 | ," |
| 1B | 550°C | ," | 1.52 | 1.57 | ," |
| 1C | ," | ," | 1.52 | 1.57 | ," |
| 2 | 500°C | 2.5 | 1.52 | 1.52 | ," |
| 2A | ," | ," | 1.52 | 1.53 | ," |
| 2B | 550°C | ," | 1.52 | 1.54 | ," |
| 2C | ," | ," | 1.52 | 1.54 | ," |
| 3 | 500°C | 4 | 1.52 | 1.56 | ," |
| 3A | ," | ," | 1.52 | 1.56 | ," |
| 3B | 550°C | ," | 1.52 | 1.56 | ," |
| 3C | ," | ," | 1.52 | 1.56 | ," |
| 4 | 500°C | 5 | 1.52 | 1.56 | ," |
| 4A | ," | ," | 1.52 | 1.57 | ," |
| 4B | 550°C | ," | 1.52 | 1.57 | ," |
| 4C | ," | ," | 1.52 | 1.57 | ," |

WHAT WE CLAIM IS:—

1. An electrode for use in an electrochemical process comprising an electrically conductive base provided over at least a portion of its outer surface with a coating comprising a mixed crystal material of tantalum oxide and iridium oxide, the proportion of tantalum to iridium calculated as metal in the material being from 1:1 to 0.34:1 by weight.

2. An electrode according to claim 1, in which the base is of a valve metal.

3. An electrode according to claim 1, in which the base is of an alloy of a valve metal with a platinum group metal.

4. An electrode according to claim 2 or claim 3, in which the valve metal is titanium.

5. An electrode according to claim 1, in which the base is of an alloy containing at least two valve metals.

6. An electrode according to claim 3, in which the alloy is of titanium containing from 0.1% to 0.2% by weight of palladium.

7. An electrode according to claim 1, comprising a base of titanium alloyed with from 0.1% to 0.2% by weight of palladium provided over from 50% to 100% of its surface with the coating comprising the mixed crystal material.

8. An electrode according to any one of claims 1 to 7, in which the coating further contains a doping oxide of a metal having a valency of less than +4, the oxide being present in an amount ranging from 0.5% to 5.0% by weight of the doping oxide and the

mixed crystal material, all the components of the percentage being calculated as metal.

9. An electrode according to claim 8, in which the metal is cobalt or an alkaline earth metal.

10. A method of preparing an electrode in accordance with claim 1, the method comprising applying to an electrically conductive electrode base a solution of suitable relative quantities of a thermally decomposable compound of tantalum and of a thermally decomposable compound of iridium, drying the coated electrode base by evaporation of the solvent and then heating the dried electrode base in the presence of oxygen to form the coating.

11. A method according to claim 10, in which the heating is effected at a temperature from 350° to 600°C.

12. A method according to claim 11, in which the temperature is from 500° to 550°C.

13. A method according to any one of claims 10 to 12, in which the base is of titanium alloyed with from 0.1% to 0.2% by weight of palladium.

14. A method according to any one of claims 10 to 13, in which the solution also contains a thermally reducible compound of a doping metal with a valency of less than +4.

15. A method according to claim 14, in which the doping metal is cobalt or calcium.

16. A method of electrowinning a metal, the method comprising passing an electric current through an anode in accordance with any one of claims 1 to 9, then through an acid aqueous

electrolyte containing the metal to be electro-won and then through a cathode to cause the metal to be deposited on the cathode.

5 17. An electrode according to claim 1, substantially as described herein with reference to any one of Examples I, III, V or VII.

18. A method according to claim 10, substantially as described herein with reference to any one of Examples I, III, V or VII.

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